

## PATENT SPECIFICATION

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(54) PROCESS FOR THE PRODUCTION OF FLAME-  
 RESISTANT FOAM RESINS WHICH CONTAIN URETHANE  
 GROUPS

(71) We, BAYER AKTIENGESELLSCHAFT a body corporate organised under the laws of Germany of 509 Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Urethane group-containing foam resins obtained by reacting polyisocyanates with polyols which contain active hydrogen atoms are widely used, e.g. in the field of insulation, for the manufacture of structural elements or for upholstery padding. The possible applications of polyurethane foams are, however, restricted by their inflammability at high temperatures and/or in the presence of fire.

It is known to produce urethane group-containing foam resins which have flame resistant properties from compounds which contain active hydrogen atoms, preferably polyols, polyisocyanates, water and/or other blowing agents in the presence of emulsifiers, auxiliary agents and catalysts as well as flame retarding additives. The function of the emulsifiers and stabilizers in the reaction mixture is to homogenize the reactants and, at the same time, to facilitate the foaming process and prevent collapse of the foam after the cessation of gas formation. The catalysts are intended to ensure that the processes taking place during formation of the foam are brought into the required equilibrium and take place at the correct velocity. A certain non-inflammability can be achieved by first adding to the starting components foaming agents which reduce the flammability of the foam. Substances which have been used for rendering foams non-flammable are compounds of phosphorus, halogens, antimony, bismuth and boron and, also, to a certain extent, nitrogen compounds. Flame-retarding additives may be subdivided into those which are built into the foam structure by their functional groups and those which, due to the absence of such groups, are merely loosely incorporated and act more as plasticizers or fillers (see Chapter 2, 3 and 10 "Flammhemmende Substanzen", Kunststoff-Handbuch, Vieweg-Höchtlen Volume XII, Polyurethane, Carl Hanser-Verlag, Munich, 1969).

The introduction of such flame retarding compounds into urethane-group-containing resins which have a low density and large surface area frequently results in a loss of desirable physical properties such as high tensile strength, shape permanence, stretchability and bearing capacity and therefore restricts the application of such foams. For example, although the introduction of a hygroscopic flame-retarding additive to a polyurethane foam reduces its flammability, it also increases its moisture absorption and therefore results in poor age-resistance properties. The application of flame-retarding additives may also result in a steep increase in internal cell structures, formation of coarse cell structure, and/or collapse of the foam. Effective fire-proofing of polyurethane foams, in contrast to the fire-proofing of compact poly-

urethanes, is difficult because the desired distribution of the additive at the gas/solid interfaces is impossible to achieve owing to the composition of the foaming mixture. It should also be pointed out here that the effective fireproofing of a polyurethane foam is not a simple function of the addition of various fireproofing agents.

Flame-resistant urethane group-containing foam resins with the desired physical properties may be produced e.g. from polyethers which contain active hydrogen atoms and in which at least 10% of the hydroxyl groups present are primary hydroxyl groups and which have a molecular weight of e.g. 750 to 10,000, preferably 4000 to 8000, and special polysiocyanates.

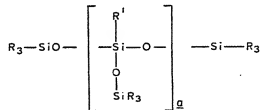
The special polysiocyanates required for this purpose are for example the so-called modified polysiocyanates, e.g. solutions of polysiocyanates which contain biuret groups in polysiocyanates which are free from biuret groups and/or solutions of polysiocyanates which contain at least two NCO groups and at least one N,N'-disubstituted aliphatic acid ester group in polysiocyanates which are free from aliphatic acid ester groups and/or solutions of reaction products of diisocyanates and divalent or higher-valent compounds which contain hydroxyl groups in polysiocyanates which are free from urethane groups and/or solutions of polysiocyanates which contain more than one NCO group and at least one isocyanuric acid ring in polysiocyanates which are free from isocyanurate groups. High flame resistance in foam resins which contain urethane groups means that they are graded as self-extinguishing according to ASTM Method D 1692-67 T.

Flame-resistant urethane group-containing foam resins with the desired physical properties which have been produced e.g. using the modified polysiocyanates have the disadvantage of having faults in the form of bubbles under the surface of the foam, which may also extend to the interior of the foam. These faults occur especially in moulded foam products produced by the process of foaming in the mould and they are a very serious disadvantage, e.g. in the manufacture of moulded parts used for the furniture industry or motor car industry because these bubbles are very clearly visible through fine quality covering materials.

It has been found that attempts to overcome this defect by using commercial polysiloxane-polyalkylene oxide copolymers do not give the desired result because the addition of even a small quantity of stabilizer results in irreversible shrinkage of the foam so that the foam becomes unusable.

According to the invention, a process for the production of non-shrinking flame-resistant foam resins which contain urethane groups has been found which is based on the use of certain siloxanes for preventing the undesirable formation of bubbles in the interior of the foam and under the surface.

This invention thus relates to a process for the production of non-flammable, non-shrinking open-celled foam resins which contain urethane groups from polyethers which contain active hydrogen atoms and preferably have a molecular weight of 750 to 10,000, polysiocyanates, water and/or organic blowing agents in the presence of silicon compounds, in which the silicon compounds are siloxanes of the following general formula



preferably used in quantities of 0.1 to 25% by weight, more preferably 0.20 to 5% by weight, based on the weight of polysiocyanate and of polyether. In the above formula, R represents an aliphatic hydrocarbon radical preferably containing less than 3 carbon atoms, preferably methyl, R' represents a monovalent aromatic radical, preferably phenyl, and a represents values of from 0 to 3; at least 70% by weight of the siloxane mixture consisting of siloxanes in which a=1 and siloxanes in which a=0 and a=2 or a=3 are present in the mixture in proportions of not more than 25% by weight, 20% by weight and 5% by weight, respectively.

The following technical advantages have surprisingly been found.

1. The siloxanes used according to the invention are substances which can be

thoroughly and rapidly mixed with the polyethers mentioned above and the other foam components. Rapid and vigorous mixing of the components brings considerable advantages, namely the fluidity of the reaction mixture and the formation of nuclei during the foaming process are greatly promoted, factors which are the precondition for optimum manufacturing results in the production of foams by a moulding process involving long flow paths or widely varying cross-sections, and, moreover, the stability of the reaction mixture is improved and, after completion of the foaming process, a fine cell structure is obtained right up to the surface of the foam in cases where foams are produced by a moulding process.

2. Highly elastic mouldings with an exceptionally good handle can be obtained using the conventional foaming conditions and foam formulations, which means that the compression characteristic is advantageously improved.

3. The siloxanes used according to the invention do not impair the efficiency of agents used for obtaining an open cell structure, which agents may be either loosely incorporated or built in chemically and can be uniformly distributed throughout the whole substance.

4. When used in the conventional foam formulations under conventional operating conditions, siloxanes according to the invention result in foams with a high flame resistance, which means that according to ASTM D 1692-67 T they are graded as self-extinguishing and in this respect they differ from the polysiloxane-polyalkylene oxide copolymers conventionally used which result in foams which are assessed as flammable according to ASTM D 1692-67 T.

The starting components used for carrying out the process according to the invention may be known aliphatic, cycloaliphatic, araliphatic or aromatic polyisocyanates, for example tetramethylene-1,4-diisocyanate; hexamethylene - 1,6 - diisocyanate; dodecane-1,12-diisocyanate; cyclohexane-1,3- and -1,4-diisocyanate and any mixtures of these isomers; 1 - isocyanato - 3,3,3 - trimethyl - 5 - isocyanatomethyl - cyclohexane; phenylene - 1,3 - and - 1,4 - diisocyanate; tolylene - 2,4 - and - 2,6 - diisocyanate and any mixtures of these isomers; hexahydrotolylene-2,4- and -2,6-diisocyanate and any mixtures of these isomers; diphenylmethane-4,4'-diisocyanate; naphthylene-1,5-diisocyanate; triphenylmethane-4,4',4''-triisocyanate; polyphenyl-poly-methylene polyisocyanates produced by the phosgenation of aniline-formaldehyde condensation products; polyisocyanates containing carbodiimide-isocyanate adducts obtained according to German Patent Specification No. 1,092,007; the diisocyanates described in U.S. Patent Specification No. 3,492,330; polyisocyanates containing allophanate groups as described in British Patent Specification No. 994,890; Belgian Patent Specification No. 761,626 and published Dutch Patent Application No. 7,102,524; polyisocyanates with isocyanurate groups as described in German Patent Specifications Nos. 1,022,789 and 1,027,394 and in German Offenlegungsschriften Nos. 1,929,034 and 2,004,048; polyisocyanates containing biuret groups as described in German Patent Specification No. 1,101,394; British Patent Specification No. 889,050 and French Patent Specification No. 7,017,514; polyisocyanates prepared by telomerisation reactions as described in Belgian Patent Specification No. 723,640; polyisocyanates containing ester groups in accordance with British Patent Specifications Nos. 956,474 and 1,072,956; aliphatic, cycloaliphatic, araliphatic or aromatic polyisocyanates mentioned by W. Siefgen in Justus Liebig's Annalen der Chemie, 562, pages 75 to 136; reaction products of the above mentioned isocyanates with acetals in accordance with German Patent Specification No. 1,072,385 and the isocyanates mentioned in German Patent Specifications Nos. 1,022,789 and 1,027,394.

Any mixtures of the above mentioned polyisocyanates may, of course, also be used.

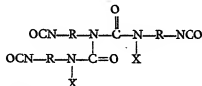
It is generally preferred to use commercially readily available polyisocyanates, e.g. tolylene-2,4- and -2,6-diisocyanate and any mixtures of these isomers as well as polyphenyl-poly-methylene-polyisocyanate which may be produced by the phosgenation of aniline-formaldehyde condensation products.

According to the invention, it is also preferred to use polyisocyanates which are solutions of so-called modified polyisocyanates, i.e. solutions of polyisocyanates containing biuret, allophanate, urethane or isocyanurate groups in polyisocyanates which are free from such groups. Preparation of these modified polyisocyanates is known *per se*. The solutions of modified polyisocyanates which are preferred for the invention generally contain 5 to 85% by weight and preferably 10 to 50% by weight of modified polyisocyanate. The unmodified polyisocyanates used are mainly tolylene-2,4- and/or -2,6-diisocyanate, which may be mixed with diphenyl-methane-4,4'-diisocyanate and its isomers.

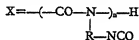
Preparation of allophanate polyisocyanates may be carried out e.g. according to

Belgian Patent Specification No. 763,529, preferably using diisocyanates such as tolylene-2,4-diisocyanate or mixtures thereof with tolylene-2,6-diisocyanate. The polyisocyanate solutions used according to the invention generally contain 5 to 85% by weight, more preferably 10 to 50% by weight, of allophanate polyisocyanate.

The modified polyisocyanates used according to the invention may also be solutions of polyisocyanates which contain biuret groups in polyisocyanates which are free from biuret groups. It is preferred to use 5 to 85% by weight solutions of biuret group-containing polyisocyanates of the following general formula:



in which R represents a preferably  $\text{C}_1$  to  $\text{C}_{12}$  alkylene radical, preferably  $\text{C}_6$  to  $\text{C}_{10}$  cycloalkylene radical, preferably  $\text{C}_6$  to  $\text{C}_{12}$  aralkylene radical or preferably  $\text{C}_6$  to  $\text{C}_{10}$  arylene radical and X represents hydrogen or the group



in which R has the meaning specified above and  $n$  represents 0 or an integer preferably 0 or an integer of from 1 to 5 in polyisocyanates which are free from biuret groups, the proportion of biuret polyisocyanates which contain more than 3 isocyanate groups, based on the total quantity of polybiuret isocyanates, preferably being at least 20% by weight. Preparation of polyisocyanates which contain biuret groups may be carried out e.g. according to British Patent Specification No. 889,050 or German Patent Specification No. 1,101,394. Preferred polyisocyanates according to the invention are solutions of biuret polyisocyanates which have been prepared by reacting tolylene-2,4- and/or -2,6-diisocyanate, diphenyl methane-4,4'-diisocyanate and/or its isomers or a polyisocyanate mixture produced by the phosgenation of aniline-formaldehyde condensation products with water or formic acid in polyisocyanates which are free from biuret groups. The polyisocyanates used according to the invention preferably contain 0.03 to 5% by weight, more particularly 0.1 to 2% by weight, of chemically bound emulsifiers. These emulsifiers should contain hydroxyl, amino, amido,  $\text{H}-\text{COOH}$ ,  $-\text{SH}$  or urethane groups and are therefore incorporated in the polyisocyanate by reaction with the isocyanate groups in accordance with German Offenlegungsschrift No. 1,963,189.

The isocyanate components used as starting material according to the invention may also be polyisocyanates which contain urethane group-containing polyisocyanates and which may be more highly branched than pure difunctional isocyanates. The isocyanates used according to the invention preferably contain 5 to 85%, more preferably 10 to 50%, of urethane group-containing isocyanates dissolved in polyisocyanates which are free from urethane groups.

Modified polyisocyanates preferably used as starting material may also be solutions of polyisocyanates which contain at least one isocyanuric acid ring in liquid polyisocyanates which are free from isocyanurate groups. Such isocyanurate group-containing polyisocyanates and processes for preparing them have been described e.g. in German Patent Specification No. 951,168 and 1,022,789; British Patent Specifications No. 821,158; 827,120; 856,372; 927,173; 920,080 and 952,931; U.S. Patent Specifications No. 3,154,522 and 2,801,244; French Patent Specification No. 1,510,342 and Belgian Patent Specification No. 718,994. The polyisocyanates which contain at least one isocyanuric acid ring are preferably polymeric tolylene diisocyanates, 2,4- or 2,6-isomers or any mixtures of these isomers, which may be mixed with 4,4'-diphenylmethane-diisocyanate or its isomers. The isocyanates used according to the invention are obtained by dissolving the polyisocyanate which contains isocyanurate groups, generally in quantities of 5 to 85% by weight based on the weight of the resulting polyisocyanate solutions, in the liquid polyisocyanates which are free from isocyanurate groups.

The polyisocyanates which are free from urethane groups, allophanate groups, isocyanurate, groups or biuret groups may be aliphatic, cycloaliphatic, aromatic or

araliphatic polyisocyanates, e.g. those described in Liebigs Annalen der Chemie, Volume 562 (1949), page 775 et seq. It is preferred to use tolylene-2,4- and/or -2,6-diisocyanate or undistilled crude mixtures of these isomers, diphenyl-methane-4,4'- and/or -2,4'-diisocyanate or the undistilled crude mixtures, naphthalene-1,5-diisocyanate, triphenyl-methane-4,4',4''-triisocyanate, 1 - isocyanato - 3,3,5 - trimethyl - 5 - isocyanatomethyl - cyclohexane, polyphenyl-polymethylene polyisocyanates produced by the phosgenation of the condensation products of aniline and/or alkyl-substituted anilines with formaldehyde or isocyanates which contain carbodiimide-isocyanate adducts as described e.g. in German Patent Specification No. 1,092,007.

Monofunctional isocyanates such as propylisocyanate, cyclohexylisocyanate, phenylisocyanate, tolylisocyanates or *p*-chlorophenylisocyanate may also be included but they should not amount to more than 20% of the isocyanate combination used according to the invention, based on the total isocyanate content.

Polyethers which contain at least two active hydrogen atoms and generally have a molecular weight of 750 to 10,000 and in which preferably at least 10% of the hydroxyl groups present are primary OH groups are also used as starting material for the process of the invention. These polyethers may be obtained e.g. by reacting compounds which contain reactive hydrogen atoms, e.g. polyalcohols, with alkylene oxides such as ethylene oxide, propylene oxide, butylene oxide, styrene oxide or epichlorohydrin, which may be followed by modification of the resulting polyethers with ethylene oxide.

Suitable polyalcohols and phenols are e.g. ethylene glycol, diethylene glycol, polyethylene glycol, propane-1,2-diol, propane-1,3-diol, butane-1,4-diol, hexane-1,6-diol, decane-1,10-diol, butyne-2-diol-1,4-glycerol, butane-2,4-diol, hexane-1,3,6-triol, trimethylolpropane, resorcinol, di-*tert*-butyl-pyrocatechol, 3-hydroxy-2-naphthol, 6,7-di-hydroxyl-1-naphthol, 2,5-dihydroxy-1-naphthol, 2,2-(*p*-hydroxyphenyl)-propane, 4-(*p*-hydroxyphenyl)-methane, tris-(hydroxyphenyl) alkanes such as tri-(hydroxyphenyl)-methane or tris-(hydroxyphenyl)-propane. Other suitable polyethers are: Adducts of 1,2-alkylene oxides with aliphatic or aromatic monoamines or polyamines, e.g. ammonia, methylamine, ethylene diamine, tetra- or hexa-methylene diamine, diethylene triamine, ethanolamine, diethanolamine, methyl-diethanolamine, triethanolamine, aminoethylpiperazine, toluidine, ortho-, meta- and para-phenylene diamine, 2,4- and 2,6-diaminotoluene, 2,6-diamino-*p*-xylene, multi-nuclear and condensed aromatic polyamines such as 1,4-naphthylene-diamine and 4,4'-diamino-azobenzene. Resinous materials of the phenol or resol type may also be used as starting materials.

All these polyethers are preferably prepared with the addition of ethylene oxide. They may also be modified by reaction with less than equivalent quantities of polyisocyanate.

The higher molecular weight polyethers used according to the invention may also be used in admixture with low molecular weight compounds (molecular weight up to 750) which contain active hydrogen atoms or in admixture (up to 50% by weight based on the polyether) with other higher molecular weight compounds which contain active hydrogen atoms. Suitable low molecular weight compounds with active hydrogen atoms are mainly compounds which contain hydroxyl groups, e.g. ethylene glycol, 1,3-butylene glycol, 1,4-butylene glycol, glycerol, trimethylolpropane, castor oil or adducts (molecular weight generally 200 to 750) of alkylene oxides such as ethylene oxide, propylene oxide or butylene oxide with such low molecular weight compounds which contain active hydrogen atoms or with water. Other suitable higher molecular weight compounds with active hydrogen atoms are known compounds such as polyesters, polyacetals, polyester amides or polycarbonates. These may be used in proportions of up to 50% by weight, based on the polyether.

The self-extinguishing polyurethane foams may be produced either by the pre-polymer process or, preferably, by the known one-shot process. In the one-shot process, the foam is produced at room temperature and/or elevated temperature by simply mixing the polyisocyanates with the polyethers, using water and/or other blowing agents, to which emulsifiers and other auxiliary agents as well as the siloxanes according to the invention may also be added. Mechanical devices are advantageously used for this purpose, e.g. those described in French Patent Specification No. 1,047,713.

Suitable emulsifiers are e.g. adducts of ethylene oxide and/or propylene oxide with hydrophobic substances which contain hydroxyl, amino or amido groups. Suitable catalysts for producing foam resins which contain urethane groups are e.g. tertiary amines and/or siloxanes, *N*-substituted aziridines, or hexahydrotriazines, which may be used in combination with organometallic compounds. Whereas amines preferentially catalyse the blowing reaction, organometallic compounds preferentially catalyse the

cross-linking reaction. To achieve reaction times which are advantageous for the foaming technique, the most suitable quantity of catalyst or catalyst mixture. The amines used according to the constitution of the selected catalyst or catalyst mixture. The amines used may be those commonly used for the production of polyurethane foams, for example dimethylbenzylamine, N-methylmorpholine, triethylenediamine, dimethylpiperazine, 1,2-dimethylimidazole, dimethylethanolamine, diethanolamine, triethanolamine, diethylaminoethanol, tetramethyl-butane-1,3-diamine, N-methyl-N'-dimethyl-aminoethyl-piperazine or pentamethylene-tetra-amine.

The silaamines used are silicon compounds which contain carbon-silicon bonds, e.g. as described in German Patent Specification No. 1,229,290, 2,2,4-Trimethyl-2-silamorpholine and 1,3-diethyl-aminomethyl-tetramethyldisiloxane are mentioned here as examples but nitrogen-containing bases such as tetraalkylammonium hydroxides as well as alkalis, alkali metal phenolates or alcoholates, e.g. sodium methylate, may be used. The organic metal compounds which may be used in combination with amines, silaamines and hexahydrotriazines in accordance with German Offenlegungsschrift No. 1,769,043 are preferably organic tin compounds, e.g. tin(II) octoate or dibutyl tin dilaurate.

Additives for regulating the cell structure, such as organic or inorganic fillers, dyes or plasticizers such as phthalic acid esters may also be used.

Foaming is preferably carried out in moulds, the reaction mixture being introduced into a mould. The material of which the mould is made may be of metal, e.g. aluminium, or a synthetic resin, e.g. epoxy resin. The foamable reaction mixture foams up in the mould and forms the moulded product. Foaming in the mould may be carried out in such a manner that the moulded product has a cell structure on its surface but it may also be carried out to produce a moulded product with a compact skin and cellular core. According to the invention, this is achieved by introducing so much foamable reaction mixture into the mould that the resulting foam just fills the mould. Alternatively, a larger quantity of foamable reaction mixture than is required for filling the interior of the mould with foam may be introduced. This method is known as "overcharging". It has already been disclosed, e.g. in U.S. Patent Specification No. 1,178,490 and 3,182,104.

Blowing agents in many cases already known *per se* are used for foaming in the mould.

According to the invention, the products produced are in particular cold hardening foams (see British Patent Specification No. 1,162,517 and German Offenlegungsschrift No. 2,153,086).

The silicones used according to the invention are known *per se* and may be prepared e.g. by the process according to German Patent Specification No. 1,046,049 or according to U.S. Patent Specification No. 3,012,052.

The foam resins according to the invention may be used for known applications, e.g. in the field of upholstery.

The invention will now be further described in the following specific examples in which parts and percentages are in all cases parts and percentages by weight unless otherwise specified.

#### Examples

The siloxanes used according to the invention are those which can be easily prepared as described in German Patent Specification No. 1,046,049. The siloxanes used in the following examples correspond to the formula on page 4 in which R = methyl and R' = phenyl and they have the following compositions:

#### Siloxane 1:

83.5 Parts by weight of the above mentioned formula in which	a=1
14.5 parts by weight of the above mentioned formula in which	a=2
2.0 parts by weight of the above mentioned formula in which	a=3.

#### Siloxane 2:

15.0 Parts by weight of the above mentioned formula in which	a=0
71.0 parts by weight of the above mentioned formula in which	a=1
12.3 parts by weight of the above mentioned formula in which	a=2
1.7 parts by weight of the above mentioned formula in which	a=3.

#### Siloxane 3:

25.0 Parts by weight of the above mentioned formula in which	a=0
74.0 parts by weight of the above mentioned formula in which	a=1
1.0 part by weight of the above mentioned formula in which	a=2.

## Example 1

## A) Preparation of the polyisocyanate

20 Parts of 1,2-propylene glycol were added to a mixture of 225 parts of a mixture of 80% by weight of tolylene-2,4-diisocyanate and 20% by weight of tolylene-2,6-diisocyanate and 274 parts by weight of diphenylmethane-4,4'-diisocyanate at 60°C, and the mixture was reacted for 30 minutes. After the addition of 1 part of  $\beta$ -phenyl-ethyl-ethyleneimine, the reaction mixture was heated to 130°C. Trimerisation which took place at this temperature was stopped after 2½ hours, when the NCO content of the reaction mixture was 26.5%, by adding 1 part of methyl p-toluenesulphonate. After dilution with 624 parts of an 80/20 mixture of tolylene-2,4- and -2,6-diisocyanate, a polyisocyanate solution was obtained which had an NCO content (%): 38.4, viscosity  $cP_{25, deg C}$ : 24, refractive index  $n_D^{20}$ : 1.5738.

B) 100 Parts by weight of a polypropylene glycol which had been started on dipropylene glycol and modified with ethylene oxide to result in 60% of primary hydroxyl end groups with OH number 28, 3.5 parts by weight of water, 0.1 part by weight of endoethylene piperazine, 0.4 part by weight of triethylamine, and 0.9 part by weight of siloxane 1 were mixed together and reacted with 47.0 parts by weight of the polyisocyanate mentioned above. A foam which had the following mechanical properties was obtained:

Density	DIN 53420	(kg/m³)	38
Tensile strength	DIN 53571	(kp/cm²)	0.8
Elongation at break	DIN 53571	(%)	150
Compression test	DIN 53577	(p/cm²)	25
Flammability according to ASTM D 1692-67 T			
Length of burnt sample/average value		(cm)	6.0
Average extinction time		(sec.)	35
Assessment		Self-extinguishing.	

## Example 2

## A) Preparation of a polyisocyanate

1.33 Parts of 1,2-propylene glycol were added to 27.5 parts of the mixture of tolylene-2,4- and -2,6-diisocyanate mentioned in Example 1 at 60°C and after a reaction time of 30 minutes, during which time the temperature rose to 80°C, 0.044 part of  $\beta$ -phenyl-ethyl-ethyleneimine was added.

Using nitrogen at protective gas, the reaction mixture was then heated to 130°C and trimerisation was stopped after a reaction time of about 5 hours at this temperature, when the NCO value was 25.8%, by adding 0.042 parts of benzoyl chloride. After dilution of the reaction mixture with 71.50 parts of a 65/35 mixture of tolylene-2,4- and -2,6-diisocyanate, 5.28 parts of 2,3-dibromopropanol were added to this solution and reacted for 2 hours at 80 to 90°C. The modified polyisocyanate solution had the following properties.

NCO content (%): 38.5, viscosity  $cP_{25, deg C}$ : 26 and refractive index  $n_D^{20}$ : 1.5690.

B) 100 Parts by weight of a polypropylene glycol which had been started on dihydroxydiphenylmethane and modified with ethylene oxide to result in about 60% of primary OH end groups with OH number 28,

3.5 parts by weight of water,  
0.1 part by weight of endoethylene piperazine,  
1.0 part by weight of N,N-dimethylbenzylamine and  
1.0 part by weight of siloxane 1

were mixed together and reacted with 44.0 parts by weight of the polyisocyanate prepared as described above. A foam resin which had the following mechanical properties was obtained.

Density	DIN 53420	(kg/m³)	40
Tensile strength	DIN 53571	(kp/cm²)	0.7
Elongation at break	DIN 53571	(%)	160
Compression test	DIN 53577	(p/cm²)	25
Flammability according to ASTM D 1692-67 T			
Length of burnt sample/average value		(cm)	3.5
Average extinction time		(sec.)	25
Assessment		Self-extinguishing.	

## Example 3

## A) Preparation of polyisocyanate

0.040 Part of a solution of water in acetone (25 g of water made up to 1000 ml with acetone) and 0.038 part of  $\beta$ -phenyl-ethyl-ethylene-imine were added to 25.0 parts of the mixture of tolylene-2,4- and -2,6-diisocyanate mentioned in Example 1 at 22°C. After a brief incubation period, the slightly exothermic trimerisation of the diisocyanate began. It was stopped after a reaction time of about 2 to 2½ hours, when the NCO content was 31% and the reaction temperature 70°C, by adding 0.024 part of methyl *p*-toluene sulphonate. 3 Parts of tripropylene glycol were added when the temperature of the reaction mixture was 80°C and reacted at that temperature for 1½ hours.

After the addition of 75 parts of an 80/20 mixture of tolylene-2,4- and -2,6-diisocyanate and vigorous homogenization of the reactants, 5.42 parts of 2,3-dibromopropanol were added to the reaction mixture at 90°C. After a reaction time of 2 hours at 90 to 100°C, the polyisocyanate combination had an NCO content (%): 38.2, viscosity  $cP_{25 \text{ deg C}}$ : 33 and refractive index  $n_D^{20}$ : 1.5790.

B) 100 Parts by weight of a polypropylene glycol which had been started on propylene glycol and modified with ethylene oxide to result in approximately 60% of primary hydroxyl end groups with OH number 28,

3.2 parts by weight of water,  
0.1 part by weight of endoethylenepiperazine,  
0.4 part by weight of triethylamine and  
1.0 part by weight of siloxane 2

were mixed together and reacted with 45.5 parts by weight of the polyisocyanate prepared as described above.

A foam resin which had the following mechanical properties was obtained:

Density	DIN 53420	(kg/m³)	35
Tensile strength	DIN 53571	(kp/cm²)	0.6
Elongation at break	DIN 53571	(%)	135
Compression test	DIN 53577	(p/cm²)	20
Flammability according to ASTM D 1692-67 T			
Length of burnt sample/average value		(cm)	6.0
Average extinction time		(sec.)	35
Assessment		Self-extinguishing.	

## Example 4

## A) Preparation of the polyisocyanate

1.96 Parts of 1,2-propylene glycol were added to 35.0 parts of the mixture of tolylene-2,4- and -2,6-diisocyanate mentioned in Example 1 at 60°C and reacted for 30 minutes, the reaction mixture heating up to 80°C during this time. After the addition of 0.037 parts of  $\beta$ -phenyl-ethyl-ethylene imine, the reaction mixture was heated to 130°C and then left at that temperature, at which trimerisation of the isocyanate mixture took place, until the NCO value was 30.0%, which took about 1 to 2 hours. After cooling to 100°C, 3.70 parts of tripropylene glycol were added and reacted at the same temperature over a period of one hour. The reaction mixture which at the end of this time had an NCO value of 23.3%, was then diluted with 65.06 parts of an 80/20 mixture of tolylene-2,4- and -2,6-diisocyanate. The resulting polyisocyanate solution had the following properties: NCO content (%): 38.9, viscosity  $cP_{25 \text{ deg C}}$ : 39, refractive index:  $n_D^{20}$ : 1.5642.

B) 100 Parts by weight of a polypropylene glycol which had been started on trimethylolpropane and modified with ethylene oxide to result in approximately 60% of primary hydroxyl end groups with OH number 28, 2.6 parts by weight of water, 0.15 parts by weight of endoethylenepiperazine, 0.40 parts by weight of tetramethylethylenediamine and 2.0 parts by weight of siloxane 3 were mixed together and reacted with 38.8 parts by weight of the polyisocyanate mentioned above.



A foam resin which had the following mechanical properties was obtained:

	Density	DIN 53420	(kg/m <sup>3</sup> )	41	
	Tensile strength	DIN 53571	(kp/cm <sup>2</sup> )	0.6	
	Elongation at break	DIN 53571	(%)	135	
5	Compression test	DIN 53577	(p/cm <sup>2</sup> )	20	5
	Flammability according to ASTM D 1692-67 T				
	Length of burner sample/average value		(cm)	4.1	
	Average extinction time		(sec.)	30	
	Assessment			Self-extinguishing.	

#### Example 5

- 10 A) If the process were carried out in the same way as is described under 7 A) but 2.03 parts of trimethylolpropane were used instead of tripropylene glycol and the reaction mixture was diluted with 66.30 parts of an 80/20 mixture of tolylene-2,4- and -2,6-diisocyanate, then the polyisocyanate solution obtained had the following properties: NCO content (%): 39.0, viscosity  $\eta_{sp}$  at 25 deg C: 58, refractive index  $n_D^{20}$ : 1.5682. 15

- B) 100 Parts by weight of a polypropylene glycol which had been started on tri-methylolpropane and modified with ethylene oxide to result in approximately 70% of primary hydroxyl end groups with OH number 32.0, 20
- 2.5 parts by weight of water,  
0.1 part by weight of endoethylenepiperazine,  
1.0 part by weight of N,N-dimethyl-benzylamine and  
1.5 parts by weight of siloxane 2

- 25 were mixed together and reacted with 37.5 parts by weight of the polyisocyanate prepared as described above. A foam resin with the following mechanical properties was obtained. 25

	Density	DIN 53420	(kg/m <sup>3</sup> )	42	
	Tensile strength	DIN 53571	(kp/cm <sup>2</sup> )	0.6	
	Elongation at break	DIN 53571	(%)	140	
30	Compression test	DIN 53577	(p/cm <sup>2</sup> )	22	30
	Flammability according to ASTM D 1692-67 T				
	Length of burnt sample/average value		(cm)	4.0	
	Average extinction time		(sec.)	40.0	
	Assessment			Self-extinguishing.	

#### Example 6

- 35 A) Preparation of polyisocyanate
- 1.54 Parts of 1,2-propylene glycol were added at 60°C to 38.46 parts of tolylene-2,4-diisocyanate in a vessel equipped with a stirrer, using nitrogen as protective gas, and the mixture was reacted for 30 minutes, during which time it heated up to 95— 40 100°C without heating from an external source. After the addition of 0.060 parts of  $\beta$ -phenyl-ethyl-ethylencimine, the reaction mixture was heated to 130°C and then left at this temperature until, after about 5 to 6 hours, the NCO value was 26.0%. Trimerisation of the polyisocyanate was then stopped by the addition of 0.038 parts of methyl-p-toluene sulphonate, and after cooling to 120°C, the reaction mixture was 45 diluted with 60.0 parts of an 80/20 mixture of tolylene-2,4- and -2,6-diisocyanate. The polyisocyanate had the following properties: NCO content (%): 39.4%, viscosity  $\eta_{sp}$  at 25 deg C: 63, refractive index  $n_D^{20}$ : 1.5721.

- B) 100 Parts by weight of a polypropylene glycol which had been started on hexane-tol and modified with ethylene oxide to result in 60% of primary hydroxyl end groups with OH number 35, 2.5 parts by weight of water, 0.1 part by weight of endoethylenepiperazine, 0.4 parts by weight of triethylamine, 0.2 parts by weight of tetramethylethylene diamine and 1.0 part by weight of siloxane 1 were mixed together and reacted with 37.0 parts by weight of the polyisocyanate prepared as described above. A foam resin with the following mechanical properties was obtained: 50

	Density	DIN 53420	(kg/m <sup>3</sup> )	42	
	Tensile strength	DIN 53571	(kp/cm <sup>2</sup> )	0.6	
	Elongation at break	DIN 53571	(%)	130	
	Compression test	DIN 53577	(p/cm <sup>2</sup> )	22	
5	Flammability according to ASTM D 1692-67 T				5
	Length of burnt sample/average value		(cm)	4.0	
	Average extinction time		(sec.)	45.0	
	Assessment			Self-extinguishing.	

## Example 7

10	A) Preparation of the polyisocyanate				10
	0.061 Parts of a solution of water in acetone (25 g of water made up to 1000 ml with acetone) and 0.058 parts of $\beta$ -phenyl-ethyl-ethylencimine were added to 38.76 parts of tolylene-2,4-diisocyanate at 25°C. The slightly exothermic trimerisation of the diisocyanate began after a brief incubation period and was stopped after about 2 hours when the NCO value had reached 31.0 to 31.3%, by the addition of 0.042 part of benzoyl chloride.				
15					15

20	The reaction mixture was then heated to 80°C and 2.33 parts of tripropylene glycol were added over a period of 10 to 15 minutes, the reaction temperature rising to 95—100°C. Stirring was continued for one hour without further heat supply and the reaction mixture was then diluted with 58.91 parts of a mixture of tolylene-2,4- and -2,6-diisocyanate (80:20% by weight). The solution of modified isocyanurate polyisocyanate in tolylene diisocyanate had the following properties: NCO content (%): 39.5, viscosity $\eta_{sp}/c$ : 54, refractive index $n_D^{25}$ : 1.5827.				

25	B) 100.0 Parts by weight of a polypropylene glycol which had been started on trimethylolpropane and modified with ethylene oxide to result in 60% of primary hydroxyl end groups with OH number 35.0, 2.5 parts by weight of water, 0.1 part by weight of endoethylenepiperazine, 0.8 parts by weight of triethylamine and 2.0 parts by weight of siloxane 2 were mixed together and reacted with 37.5 parts by weight of the polyisocyanate mentioned above. A foam resin with the following mechanical properties was obtained:				25
30					30

	Density	DIN 53420	(kg/m <sup>3</sup> )	43	
	Tensile strength	DIN 53571	(kp/cm <sup>2</sup> )	0.6	
	Elongation at break	DIN 53571	(%)	135	
	Compression test	DIN 53577	(p/cm <sup>2</sup> )	25	
35	Flammability according to ASTM D 1692-67 T				35
	Length of burnt sample/average value		(cm)	4.0	
	Average extinction time		(sec.)	42.0	
	Assessment			Self-extinguishing.	

## Example 8

40	A) Preparation of the polyisocyanate				40
	5 Parts of 2,3-dibromopropanol were added to 95 parts of the modified isocyanurate polyisocyanate described in Example 4 in tolylene diisocyanate at 90°C and the mixture was reacted at this temperature for 2 hours. The resulting polyisocyanate solution had the following properties: NCO content (%): 36.0, viscosity $\eta_{sp}/c$ : 81, refractive index $n_D^{25}$ : 1.5858.				
45					45

50	B) 100.0 Parts by weight of a polypropylene glycol which had been started on glycerol and modified with ethylene oxide to result in 60% of primary hydroxyl end groups with OH number 35.0, 2.5 parts by weight of water, 0.1 part by weight of endoethylenepiperazine, 0.5 parts by weight of tetramethyl-ethylenediamine and 1.8 parts by weight of siloxane 3 were mixed together and reacted with 37.5 parts by weight of the polyisocyanate prepared as described above.				50
	A foam resin with the following mechanical properties was obtained:				

	Density	DIN 53420	(kg/m <sup>3</sup> )	43	
	Tensile strength	DIN 53571	(kp/cm <sup>2</sup> )	0.7	
55	Elongation at break	DIN 53571	(%)	130	55
	Compression test	DIN 53577	(p/cm <sup>2</sup> )	22	
	Flammability according to ASTM D 1692-67 T				
	Length of burnt sample/average value		(cm)	3.0	
	Average extinction time		(sec.)	25.0	
60	Assessment			Self-extinguishing.	60

## Example 9

## A) Preparation of the polyisocyanate

20 Parts of 1,2-propylene glycol were added at 60°C to a mixture of 225 parts of a mixture of 80% by weight of tolylene-2,4-diisocyanate and 20% by weight of tolylene-2,6-diisocyanate and 275 parts of diphenylmethane-4,4'-diisocyanate and reacted for 30 minutes. After the addition of 1 part of  $\beta$ -phenyl-ethylencimine, the reaction mixture was heated to 130°C. The trimerisation which took place at this temperature was stopped after 2½ hours, when the NCO content of the reaction mixture was 26.5%, by adding 1 part of methyltoluenesulphonate. After dilution with 624 parts of an 80/20 mixture of tolylene-2,4- and -2,6-diisocyanate, a polyisocyanate solution which had the following properties was obtained: NCO content (%): 38.4, viscosity  $c_{25} \text{ deg c}$ : 24, refractive index  $n_D^{25}$ : 1.5738.

B) 100.0 Parts by weight of a polypropylene glycol which had been started on sorbitol and modified with ethylene oxide to result in more than 10% of primary hydroxyl end groups with OH number 35, 2.5 parts by weight of water, 0.1 part by weight of endoethylenepiperazine, 0.3 parts by weight of N,N-dimethyl-benzylamine and 2.0 parts by weight of siloxane 1 were mixed together and reacted with 34.5 parts by weight of the polyisocyanate mentioned above.

A foam resin with the following mechanical properties was obtained:

20	Density	DIN 53420	(kg/m <sup>3</sup> )	45	20
	Tensile strength	DIN 53571	(kp/cm <sup>2</sup> )	0.5	
	Elongation at break	DIN 53571	(%)	160	
	Compression test	DIN 53577	(p/cm <sup>2</sup> )	20	
25	Flammability according to ASTM D 1692-67 T				25
	Length of burnt sample/average value		(cm)	4.5	
	Average extinction time		(sec.)	42.0	
	Assessment		Self-extinguishing.		

## Example 10

## A) Preparation of the polyisocyanate

30 154 Parts of 1,2-propylene glycol were added to 38.46 parts of tolylene-2,4-diisocyanate at 60°C in a vessel equipped with stirrer, using nitrogen as protective gas, and the mixture was reacted for 30 minutes, during which time it heated up to 95—100°C without heating from an external source. After the addition of 0.060 parts of  $\beta$ -phenyl-ethyl-ethylencimine, the reaction mixture was heated to 130°C and left at this temperature until, after about 5 to 6 hours, the NCO value is 26.0%. Trimerisation of polyisocyanate was then stopped by the addition of 0.038 parts of methyl *p*-toluene sulphonate and after cooling the reaction mixture to 120°C it was diluted with 60.0 parts of an 80/20 mixture of tolylene-2,4- and -2,6-diisocyanate. The reaction mixture had the following properties: NCO content (%): 39.4, viscosity  $c_{25} \text{ deg c}$ : 63, refractive index:  $n_D^{25}$ : 1.5721.

B) 100 Parts by weight of a polypropylene glycol which had been started on trimethylolpropane and modified with ethylene oxide to result in about 40% of primary hydroxyl end groups with OH number 20, 2.5 parts by weight of water, 0.20 parts by weight of endoethylenepiperazine, 0.3 parts by weight of N,N-dimethyl-benzylamine and 1.2 parts by weight of siloxane 1 were mixed together and reacted with 35.0 parts by weight of the polyisocyanate mentioned above.

A foam resin with the following mechanical properties was obtained:

50	Density	DIN 53420	(kg/m <sup>3</sup> )	45	50
	Tensile strength	DIN 53571	(kp/cm <sup>2</sup> )	0.6	
	Elongation at break	DIN 53571	(%)	130	
	Compression test	DIN 53577	(p/cm <sup>2</sup> )	25	
55	Flammability according to ASTM D 1692-67 T				55
	Length of burnt sample/average value		(cm)	5.0	
	Average extinction time		(sec.)	30.0	
	Assessment		Self-extinguishing.		

## Example 11

100 Parts by weight of a polypropylene glycol which had been started on dipropylene glycol and modified with ethylene oxide to result in 60% of primary hydroxyl end groups with OH number 28, 3.5 parts by weight of water, 0.1 part by

weight of endoethylenepiperazine, 0.6 parts by weight of triethylamine and 1.2 parts by weight of siloxane 1 were mixed together and reacted with 45.5 parts by weight of a polyisocyanate containing biuret groups, which polyisocyanate had been prepared by reacting a mixture of toluene-2,4- and -2,6-diisocyanate (ratio of isomers 65:35% by weight) and water (NCO content 38.5%).

A foam resin with the following mechanical properties was obtained.

5	Density	DIN 53420	(kg/m <sup>3</sup> )	35	5
	Tensile strength	DIN 53571	(kp/cm <sup>2</sup> )	0.6	
	Elongation at break	DIN 53571	(%)	150	
10	Compression test	DIN 53577	(p/cm <sup>2</sup> )	25	10
	Flammability according to ASTM D 1692-67 T				
	Length of burnt sample/average value		(cm)	6.0	
	Average extinction time		(sec.)	50.0	
	Assessment			Self-extinguishing.	

#### Example 12

100 Parts by weight of a polypropylene glycol which had been started on dihydroxydiphenylmethane and modified with ethylene oxide to result in approximately 60% of primary OH end groups with OH number 28, 3.5 parts by weight of water, 0.1 part by weight of endoethylenepiperazine, 0.6 parts by weight of triethylamine and 1.2 parts by weight of siloxane 1 were mixed together and reacted with 45.5 parts by weight of a biuret polyisocyanate which had been prepared by reacting a mixture of toluene-2,4- and -2,6-diisocyanate (ratio of isomers 80:20% by weight) and water (NCO content) 38.5%). A foam resin with the following mechanical properties was obtained:

25	Density	DIN 53420	(kg/m <sup>3</sup> )	35	25
	Tensile strength	DIN 53571	(kp/cm <sup>2</sup> )	0.7	
	Elongation at break	DIN 53571	(%)	160	
	Compression test	DIN 53577	(p/cm <sup>2</sup> )	23	
	Flammability according to ASTM D 1692-67 T				
30	Length of burnt sample/average value		(cm)	5.7	30
	Average extinction time		(sec.)	47.0	
	Assessment			Self-extinguishing.	

#### Example 13

100 Parts by weight of a polypropylene glycol which had been started on trimethylolpropane and modified with ethylene oxide to result in approximately 60% of primary hydroxyl end groups with OH number 20, 3.5 parts by weight of water, 0.1 part by weight of endoethylenepiperazine, 5.0 parts by weight of trichloroethylphosphate and 1.0 part by weight of siloxane 1 were mixed together and reacted with 43.0 parts by weight of a biuret polyisocyanate which had been prepared by reacting toluene-2,4-diisocyanate with water (NCO content 38.5%).

A foam resin with the following mechanical properties was obtained:

45	Density	DIN 53420	(kg/m <sup>3</sup> )	37	45
	Tensile strength	DIN 53571	(kp/cm <sup>2</sup> )	0.6	
	Elongation at break	DIN 53571	(%)	140	
	Compression test	DIN 53577	(p/cm <sup>2</sup> )	23	
	Flammability according to ASTM D 1692-67 T				
	Length of burnt sample/average value		(cm)	3.0	
	Average extinction time		(sec.)	25.0	
	Assessment			Self-extinguishing.	

#### Example 14

100 Parts by weight of a polypropylene glycol which had been started on trimethylolpropane and modified with ethylene oxide to result in approximately 70% of primary hydroxyl end groups with OH number 32, 2.5 parts by weight of water, 0.1 part by weight of endoethylenepiperazine, 1.0 part by weight of N,N-dimethylbenzylamine and 2.5 parts by weight of siloxane 1 were mixed together and reacted with 38.0 parts by weight of a biuret polyisocyanate which had been prepared by re-

acting a mixture of tolylene-2,4- and -2,6-diisocyanate (ratio of isomers 65:35%) and water (NCO content 38.5%).

A foam resin with the following mechanical properties was obtained:

5	Density	DIN 53420	(kg/m <sup>3</sup> )	40	
	Tensile strength	DIN 53571	(kp/cm <sup>2</sup> )	0.7	5
	Elongation at break	DIN 53571	(%)	130	
	Compression test	DIN 53577	(p/cm <sup>2</sup> )	25	
	Flammability according to ASTM D 1692-67 T				
	Length of burnt sample/average value		(cm)	7.0	
10	Average extinction time		(sec.)	60.0	10
	Assessment		Self-extinguishing.		

#### Example 15

100 Parts by weight of a polypropylene glycol which had been started on trimethylolpropane and modified with ethylene oxide to result in approximately 60% of primary hydroxyl end groups with OH number 48, 2.5 parts by weight of water, 0.1 part by weight of endoethylenepiperazine, 0.3 parts by weight of N,N-dimethylbenzylamine and 0.2 parts by weight of siloxane 1 were mixed together and reacted with 38.0 parts by weight of a biuret polyisocyanate which had been prepared by reacting a mixture of tolylene-2,4- and -2,6-diisocyanate (ratio of isomers 80:20% by weight) and water (NCO content 38.5%).

A foam resin with the following mechanical properties was obtained:

25	Density	DIN 53420	(kg/m <sup>3</sup> )	42	
	Tensile strength	DIN 53571	(kp/cm <sup>2</sup> )	0.7	
	Elongation at break	DIN 53571	(%)	120	
	Compression test	DIN 53577	(p/cm <sup>2</sup> )	25	25
	Flammability according to ASTM D 1692-67 T				
	Length of burnt sample/average value		(cm)	6.0	
	Average extinction time		(sec.)	35	
	Assessment		Self-extinguishing.		

#### Example 16

100 Parts by weight of a polypropylene glycol which had been started on glycerol and modified with ethylene oxide to result in 28% of primary hydroxyl end groups with OH number 56, 2.5 parts by weight of water, 0.20 parts by weight of endoethylenepiperazine, 0.1 part by weight of pentamethyldiethylenetriamine and 1.0 part by weight of siloxane 1 were mixed together and reacted with 42.0 parts by weight of a biuret polyisocyanate which had been prepared by reacting a mixture of tolylene-2,4- and -2,6-diisocyanate (ratio of isomer 65:35% by weight) with water (NCO content 38.5%).

A foam resin with the following mechanical properties was obtained:

40	Density	DIN 53420	(kg/m <sup>3</sup> )	45	40
	Tensile strength	DIN 53571	(kp/cm <sup>2</sup> )	0.7	
	Elongation at break	DIN 53571	(%)	120	
	Compression test	DIN 53577	(p/cm <sup>2</sup> )	30	
	Flammability according to ASTM D 1692-67 T				
45	Length of burnt sample/average value		(cm)	4.0	45
	Average extinction time		(sec.)	38	
	Assessment		Self-extinguishing.		

#### Example 17

100 Parts by weight of a polypropylene glycol which had been started on glycerol and modified with ethylene oxide to result in 60% of primary hydroxyl end groups with OH number 35, 2.5 parts by weight of water, 0.1 part by weight of endoethylenepiperazine, 0.5 parts by weight of tetramethylethylenediamine and 1.2 parts by weight of siloxane 3 were mixed together and reacted with 38.0 parts by weight of a biuret polyisocyanate which had been prepared by reacting a mixture of tolylene-2,4- and -2,6-diisocyanate (ratio of isomers 80:20% by weight) with water (NCO content 38.5%).

A foam resin with the following mechanical properties was obtained:

	Density	DIN 53420	(kg/m <sup>3</sup> )	40	
	Tensile strength	DIN 53571	(kp/cm <sup>2</sup> )	0.7	
	Elongation at break	DIN 53571	(%)	130	
5	Compression test	DIN 53577	(p/cm <sup>2</sup> )	30	5
	Flammability according to ASTM D 1692-67 T				
	Length of burnt sample/average value		(cm)	3.5	
	Average extinction time		(sec.)	42	
	Assessment			Self-extinguishing.	

10	Example 18					10
	100 Parts by weight of a polypropylene glycol which had been started on glycerol and modified with ethylene oxide to result in approximately 60% of primary hydroxyl end groups with OH number 48, 2.5 parts by weight of water, 0.1 part by weight of endoethylenepiperazine, 1.0 part by weight of triethylamine, 1.5 parts by weight of butane-1,4-diol and 1.0 part by weight of siloxane 1 were reacted with 40.5 parts by weight of a biuret polyisocyanate which had been prepared by reacting a mixture of tolylene-2,4- and -2,6-diisocyanate (ratio of isomers 80 to 20% by weight) and water (NCO content 38.5%).					15

A foam resin with the following mechanical properties was obtained:

20	Density	DIN 53420	(kg/m <sup>3</sup> )	48	20
	Tensile strength	DIN 53571	(kp/cm <sup>2</sup> )	0.9	
	Elongation at break	DIN 53571	(%)	130	
	Compression test	DIN 53577	(p/cm <sup>2</sup> )	28	
	Flammability according to ASTM D 1692-67 T				
25	Length of burnt sample/average value		(cm)	3.5	25
	Average extinction time		(sec.)	35	
	Assessment			Self-extinguishing.	

30	Example 19					30
	100 Parts by weight of a polypropylene glycol which had been started on di-propylene glycol and modified with ethylene oxide to result in approximately 60% of primary hydroxyl end groups with OH number 28, 2.5 parts by weight of water, 0.1 part by weight of endoethylenepiperazine, 0.5 parts by weight of tetramethylethylenediamine, 1.5 part by weight of tripropylene glycol and 2.0 parts by weight of siloxane 2 were reacted with 41.5 parts by weight of a biuret polyisocyanate which had been prepared by reacting a mixture of tolylene-2,4- and -2,6-diisocyanate (ratio of isomers 80:20% by weight and water (NCO content 38.5%).					35

A foam resin with the following mechanical properties was obtained:

40	Density	DIN 53420	(kg/m <sup>3</sup> )	45	
	Tensile strength	DIN 53571	(kp/cm <sup>2</sup> )	0.8	
	Elongation at break	DIN 53571	(%)	120	40
	Compression test	DIN 53577	(p/cm <sup>2</sup> )	30	
	Flammability according to ASTM D 1692-67 T				
	Length of burnt sample/average value		(cm)	3.7	
	Average extinction time		(sec.)	28	
45	Assessment			Self-extinguishing.	45

50	Example 20					50
	100 Parts by weight of a polypropylene glycol which had been started on trimethylolpropane and modified with ethylene oxide to result in approximately 75% of primary hydroxyl end groups with OH number 35, 2.5 parts by weight of water, 0.1 part by weight of endoethylenepiperazine, 1.5 parts by weight of N,N-dimethylbenzylamine, 1.0 part by weight of diethyleneglycol and 1.5 parts by weight of siloxane 1 were reacted with 41.5 parts by weight of a biuret polyisocyanate which had been prepared by reacting tolylene-2,4-diisocyanate, and water (NCO content 38.5%).					

A foam resin with the following mechanical properties was obtained:

	Density	DIN 53420	(kg/m <sup>3</sup> )	45	
	Tensile strength	DIN 53571	(kp/cm <sup>2</sup> )	0.9	
	Elongation at break	DIN 53571	(%)	130	
5	Compression test	DIN 53577	(p/cm <sup>2</sup> )	32	5
	Flammability according to ASTM D 1692-67 T				
	Length of burnt sample/average value		(cm)	3.5	
	Average extinction time		(sec.)	30.0	
	Assessment		Self-extinguishing.		

10	Example 21					10
	100 Parts by weight of a polypropylene glycol which had been started on glycerol and modified with ethylene oxide to result in approximately 65% of primary hydroxyl end groups with OH number 30, 2.5 parts by weight of water, 0.1 part by weight of endoethylenepiperazine, 0.8 parts by weight of butane-1,4-diol, 0.2 parts by weight of tetramethylenediamine and 1.8 parts by weight of siloxane 1 were reacted with 40.5 parts by weight of a biuret polyisocyanate which had been prepared by reacting tolylene-2,4-diisocyanate and water (NCO content 38.5%).					
15						15

A foam resin with the following mechanical properties was obtained:

	Density	DIN 53420	(kg/m <sup>3</sup> )	46	
	Tensile strength	DIN 53571	(kp/cm <sup>2</sup> )	0.7	
	Elongation at break	DIN 53571	(%)	120	
	Compression test	DIN 53577	(p/cm <sup>2</sup> )	30	
	Flammability according to ASTM D 1692-67 T				
	Length of burnt sample/average value		(cm)	4.2	
25	Average extinction time		(sec.)	30	25
	Assessment		Self-extinguishing.		

	Example 22					
	100 Parts by weight of a polypropylene glycol which had been started on trimethylolpropane and modified with ethylene oxide to result in approximately 60% of primary hydroxyl end groups with OH number 35, 3.0 parts by weight of water, 0.2 parts by weight of endoethylenepiperazine, 1.0 part by weight of triethylamine and 1.0 part by weight of siloxane 1 were reacted with 48.5 parts by weight of a biuret polyisocyanate which had been prepared by reacting a mixture of diphenylmethane-4,4'- and -2,4'-diisocyanate (ratio of isomers 60:40% by weight) and water (NCO content 30.0%).					
30						30
35						35

A foam resin with the following mechanical properties was obtained:

	Density	DIN 53420	(kg/m <sup>3</sup> )	42	
	Tensile strength	DIN 53571	(kp/cm <sup>2</sup> )	1.0	
	Elongation at break	DIN 53571	(%)	140	
40	Compression test	DIN 53577	(kp/cm <sup>2</sup> )	38	40
	Flammability according to ASTM D 1692-67 T				
	Length of burnt sample/average value		(cm)	5.3	
	Average extinction time		(sec.)	40	
	Assessment		Self-extinguishing.		

	Example 23					
	100.0 Parts by weight of a polypropylene glycol which had been started on hexanetriol and modified with ethylene oxide to result in approximately 60% of primary hydroxyl end groups with OH number 35.0, 2.5 parts by weight of water, 0.1 part by weight of endoethylenepiperazine, 0.7 parts by weight of N-ethylmorpholine and 0.20 parts by weight of siloxane 1 were mixed together and reacted with 38.0 parts by weight of an isocyanate adduct (NCO content 35%) obtained from trimethylolpropane and tolylene-2,4- and -2,6-diisocyanate (ratio of isomers 80:20% by weight).					
50						50

A foam resin with the following mechanical properties was obtained:

55	Density	DIN 53420	(kg/m <sup>3</sup> )	43	55
	Tensile strength	DIN 53571	(kp/cm <sup>2</sup> )	0.7	
	Elongation at break	DIN 53571	(%)	130	
	Compression test	DIN 53577	(p/cm <sup>2</sup> )	25	
	Flammability according to ASTM D 1692-67 T				
60	Length of burnt sample/average value		(cm)	3.5	60
	Average extinction time		(sec.)	28	
	Assessment		Self-extinguishing.		

## Example 24

100.0 Parts by weight of a polypropylene glycol which had been started on glycerol and modified with ethylene oxide to result in approximately 60% of primary hydroxyl end groups with OH number 35.0, 2.5 parts by weight of water, 0.18 parts by weight of endoethylenepiperazine, 0.5 parts by weight of tetramethylethylenediamine and 3.0 parts by weight of siloxane 1 were mixed together and reacted with 38.0 parts by weight of an isocyanate adduct (NCO content (35%) obtained from trimethylolpropane and tolylene-2,4- and -2,6-diisocyanate (ratio of isomers 80:20% by weight).

A foam resin with the following mechanical properties was obtained:

Density	DIN 53420	(kg/m <sup>3</sup> )	44
Tensile strength	DIN 53571	(kp/cm <sup>2</sup> )	0.6
Elongation at break	DIN 53571	(%)	120
Compression test	DIN 53577	(p/cm <sup>2</sup> )	25
Flammability according to ASTM D 1692-67 T			
Length of burnt sample/average value		(cm)	4.0
Average extinction time		(sec.)	35
Assessment		Self-extinguishing.	

## Example 25

100.0 Parts by weight of a polypropylene glycol which had been started on trimethylolpropane and modified with ethylene oxide to result in approximately 70% of primary hydroxyl end groups with OH number 32.0, 2.5 parts by weight of water, 0.15 parts by weight of endoethylenepiperazine, 1.0 part by weight of N,N-dimethylbenzylamine and 1.3 parts by weight of siloxane 3 were mixed together and reacted with 35.0 parts by weight of an isocyanate adduct (NCO content 35%) prepared from trimethylolpropane and tolylene-2,4- and -2,6-diisocyanate (ratio of isomers 80:20% by weight).

A foam resin with the following mechanical properties was obtained:

Density	DIN 53420	(kg/m <sup>3</sup> )	44
Tensile strength	DIN 53571	(kp/cm <sup>2</sup> )	0.7
Elongation at break	DIN 53571	(%)	135
Compression test	DIN 53577	(p/cm <sup>2</sup> )	28
Flammability according to ASTM D 1692-67 T			
Length of burnt sample/average value		(cm)	4.5
Average extinction time		(sec.)	35
Assessment		Self-extinguishing.	

## Example 26

100.0 Parts by weight of a polypropylene glycol which had been started on propylene glycol and modified with ethylene oxide to result in approximately 60% of primary hydroxyl end groups with OH number 28, 3.5 parts by weight of water, 0.1 part by weight of endoethylenepiperazine, 3.25 parts by weight of diisopropanolamine and 0.80 parts by weight of siloxane 1 were mixed together and reacted with 55.60 parts by weight of an isocyanate adduct (NCO content 35%) prepared from trimethylolpropane and tolylene-2,4- and -2,6-diisocyanate (ratio of isomers 80:20% by weight).

A foam resin with the following mechanical properties was obtained:

Density	DIN 53420	(kg/m <sup>3</sup> )	39
Tensile strength	DIN 53571	(kp/cm <sup>2</sup> )	1.1
Elongation at break	DIN 53571	(%)	140
Compression test	DIN 53577	(p/cm <sup>2</sup> )	30
Flammability according to ASTM D 1692-67 T			
Length of burnt sample/average value		(cm)	5.7
Average extinction time		(sec.)	50
Assessment		Self-extinguishing.	

## Example 27

100.0 Parts by weight of a polypropylene glycol which had been started on glycerol and modified with ethylene oxide to result in approximately 70% of primary hydroxyl end groups with OH number 32, 2.5 parts by weight of water, 0.2 parts by weight of endoethylenepiperazine, 1.0 part by weight of N,N-dimethylbenzylamine,



1.5 parts by weight of diethylene glycol, 3.0 parts by weight of monofluorotrichloromethane and 1.2 parts by weight of siloxane 1 were reacted with 37.5 parts by weight of an isocyanate adduct (NCO content 35%) which had been prepared from trimethylolpropane and tolylene-2,4- and -2,6-diisocyanate (ratio of isomers 80:20% by weight).

A foam resin with the following mechanical properties was obtained:

Density	DIN 53420	(kg/m <sup>3</sup> )	43
Tensile strength	DIN 53571	(kp/cm <sup>2</sup> )	0.6
Elongation at break	DIN 53571	(%)	135
Compression test	DIN 53577	(p/cm <sup>2</sup> )	35
Flammability according to ASTM D 1692-67 T			
Length of burnt sample/average value		(cm)	3.0
Average extinction time		(sec.)	30
Assessment			Self-extinguishing.

#### Example 28

A) 100.0 Parts by weight of a polypropylene glycol which had been started on hexanetriol and modified with ethylene oxide to result in approximately 60% of primary hydroxyl end groups with OH number 35.0, 2.5 parts by weight of water, 0.15 parts by weight of endoethylenepiperazine, 0.7 parts by weight of N-ethylmorpholine and 1.0 part by weight of siloxane 3 were mixed together and reacted with 40.0 parts by weight of an allophanate polyisocyanate (NCO content 35.1%).

#### B) Preparation of the polyisocyanate

134 Parts of trimethylolpropane were added over a period of about one hour to a mixture of tolylene-2,4- and -2,6-diisocyanate (ratio of isomers 80:20) which had been introduced into a reaction vessel and heated to 80°C. On addition of the trimethylolpropane, the reaction mixture heated up to 114°C. When the NCO content had reached a level of 41.3%, immediately after completion of the addition of trimethylolpropane, the reaction mixture was heated to 150°C and left at this temperature for 20 hours. The resulting product was a solution of an allophanate polyisocyanate in a mixture of tolylene diisocyanate isomers, NCO content 38.1%, viscosity at 25°C 77.

100 Parts of 2,3-dibromopropanol-1 were added to 1900 parts of this solution at 80°C and reacted for 2½ hours at 90°C. The modified allophanate polyisocyanate in the isomeric tolylene diisocyanate mixture had an NCO content of 35.1%, a viscosity of 118 cP<sub>25°C</sub> and a solids content of 41%.

A foam resin with the following mechanical properties was obtained:

Density	DIN 53420	(kg/m <sup>3</sup> )	50
Tensile strength	DIN 53571	(kp/cm <sup>2</sup> )	0.8
Elongation at break	DIN 53571	(%)	120
Compression test	DIN 53577	(p/cm <sup>2</sup> )	35
Flammability according to ASTM D 1692-67 T			
Length of burnt sample/average value		(cm)	3.0
Average extinction time		(sec.)	25
Assessment			Self-extinguishing.

#### Example 29

A) 100.0 Parts by weight of a polypropylene glycol which had been started on glycerol and modified with ethylene oxide to result in 60% of primary hydroxyl end groups with OH number 35.0, 2.5 parts by weight of water, 0.1 part by weight of endoethylenepiperazine, 0.5 parts by weight of tetramethylethylenediamine and 1.0 part by weight of siloxane 2 were mixed together and reacted with 40.0 parts by weight of an allophanate polyisocyanate (NCO content 35.1%).

#### B) Preparation of the polyisocyanate

134 Parts of trimethylolpropane were added over a period of about one hour to a mixture of tolylene-2,4- and -2,6-diisocyanate (ratio of isomers 80:20) which had been introduced into a reaction vessel and heated to 80°C. The reaction mixture heated up to 114°C. When the NCO content reached 41.3%, immediately after completion of the addition of trimethylolpropane, the reaction mixture was heated to 150°C and left at this temperature for 20 hours. The resulting product was a solution

of an allophanate polyisocyanate in a mixture of tolylene diisocyanate isomers with an NCO content of 38.1%, and a viscosity of 77 cP<sub>25 deg C</sub>.

100 Parts of 2,3-dibromopropanol-1 were added to 1900 parts of this solution at 80°C and reacted for 2½ hours at 90°C. The modified allophanate polyisocyanate in the mixture of tolylene diisocyanate isomers had an NCO content of 35.1%, a viscosity of 118 cP<sub>25 deg C</sub> and a solids content of 41%.

A foam resin with the following mechanical properties was obtained:

Density	DIN 53420	(kg/m³)	50	
Tensile strength	DIN 53571	(kp/cm²)	0.8	
Elongation at break	DIN 53571	(%)	130	10
Compression test	DIN 53577	(p/cm²)	30	
Flammability according to ASTM D 1692-67 T				
Length of burnt sample/average value		(cm)	3.6	
Average extinction time		(sec.)	28	
Assessment		Self-extinguishing.		15

#### Example 30

A) 100.0 Parts by weight of a polypropylene glycol which had been started on trimethylolpropane and modified with ethylene oxide to result in approximately 60% primary hydroxyl end groups with OH number 35, 2.5 parts by weight of water, 0.2 parts by weight of endoethylenepiperazine, 1.0 part by weight of dimethylbenzylamine and 1.0 part by weight of siloxane 1 were mixed together and reacted with 38.0 parts by weight of an allophanate polyisocyanate (NCO content 35.1%).

B) Preparation of the polyisocyanate

134 Parts of trimethylolpropane were added over a period of about one hour to a mixture of tolylene-2,4- and -2,6-diisocyanate (ratio of isomers 80:20) which had been introduced into a reaction vessel and heated to 80°C, the reaction mixture heating up to 114°C. When the NCO content reached a value of 41.3%, immediately after completion of the addition of trimethylolpropane, the reaction mixture was heated to 150°C and kept at this temperature for 20 hours. The resulting product was a solution of an allophanate polyisocyanate in a mixture of tolylene diisocyanate isomers, NCO content 38.1%, viscosity 77 cP<sub>25 deg C</sub>.

A foam resin with the following mechanical properties was obtained:

Density	DIN 53420	(kg/m³)	48	
Tensile strength	DIN 53571	(kp/cm²)	0.8	
Elongation at break	DIN 53571	(%)	120	35
Compression test	DIN 53577	(p/cm²)	35	
Flammability according to ASTM D 1692-67 T				
Length of burnt sample/average value		(cm)	4.0	
Average extinction time		(sec.)	42	
Assessment		Self-extinguishing.		40

#### Example 31

A) 100.0 Parts by weight of a polypropylene glycol which had been started on dipropylene glycol and modified with ethylene oxide to result in 60% of primary hydroxyl end groups with OH number 28.0, 2.5 parts by weight of water, 0.1 part by weight of endoethylenepiperazine, 0.4 parts by weight of N-ethylmorpholine, 0.4 parts by weight of triethylamine and 1.3 parts by weight of siloxane 1 were mixed together and reacted with 37.0 parts by weight of an allophanate polyisocyanate (NCO content 35.1%).

B) Preparation of the polyisocyanate

134 Parts of trimethylolpropane were added over a period of about one hour to a mixture of tolylene-2,4- and -2,6-diisocyanate (ratio of isomers 80:20) which had been heated to 80°C, the reaction mixture heating up to 114°C. When the NCO content reached a value of 41.3%, immediately after completion of the addition of trimethylolpropane, the reaction mixture was heated to 150°C and left at this temperature for 20 hours. The resulting product was a solution of an allophanate polyisocyanate in a mixture of tolylene diisocyanate isomers, NCO content 38.1%, viscosity 77 cP<sub>25 deg C</sub>.

100 Parts of 2,3-dibromopropanol-1 were added to 1900 parts of this solution at 80°C and reacted for 2½ hours at 90°C. The modified allophanate polyisocyanate in

the mixture of tolylene diisocyanate isomers had an NCO content of 35.1%, a viscosity of 118 cP<sub>25</sub>,  $\eta_{sp}/c$  and a solids content of 41%.

A foam resin with the following mechanical properties was obtained:

5	Density	DIN 53420	(kg/m <sup>3</sup> )	42	
	Tensile strength	DIN 53571	(kp/cm <sup>2</sup> )	0.7	5
	Elongation at break	DIN 53571	(%)	130	
	Compression test	DIN 53577	(p/cm <sup>2</sup> )	30	
	Flammability according to ASTM D 1692-67 T				
	Length of burnt sample/average value		(cm)	4.4	
10	Average extinction time		(sec.)	30	10
	Assessment		Self-extinguishing.		

#### Example 32

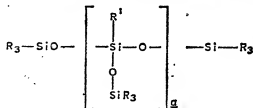
100 Parts by weight of a polypropylene glycol which had been started on trimethylolpropane and modified with ethylene oxide to result in approximately 60% of primary hydroxyl end groups with OH number 35, 3.0 parts by weight of water, 0.2 parts by weight of endoethylenepiperazine, 0.2 parts by weight of tetramethylethylenediamine, 5.0 parts by weight of trichloroethylphosphate and 1.0 part by weight of siloxane 1 were mixed together and reacted with 40.5 parts by weight of a mixture consisting of 60 parts by weight of tolylene-2,4- and -2,6-diisocyanate (ratio of isomer 65:35) and 40 parts by weight of a polyphenylpolymethylene polyisocyanate (NCO content 31%).

A foam resin with the following mechanical properties was obtained:

25	Density	DIN 53420	(kg/m <sup>3</sup> )	35	
	Tensile strength	DIN 53571	(kp/cm <sup>2</sup> )	0.5	
	Elongation at break	DIN 53571	(%)	90	25
	Compression test	DIN 53577	(p/cm <sup>2</sup> )	18	
	Flammability according to ASTM D 1692-67 T				
	Length of burnt sample/average value		(cm)	4.9	
30	Average extinction time		(sec.)	35	30
	Assessment		Self-extinguishing.		

#### WHAT WE CLAIM IS:—

1. A process for the production of an open-celled flame-resistant foam resin which contains urethane groups, from a polyether which contains active hydrogen atoms, a polyisocyanate, water and/or an organic blowing agent in the presence of a silicon compound, in which the silicon compound is a siloxane of the general formula



in which R represents an aliphatic hydrocarbon radical, R' represents a monovalent aromatic radical and a represents 0 or an integer of from 1 to 3, at least 70% by weight of the siloxane mixture consisting of siloxanes in which a=1 while siloxanes in which a=0, a=2 and a=3 are present in the mixture in proportions of not more than 25% by weight, 20% by weight and 5% by weight, respectively.

2. A process as claimed in claim 1 in which between 0.1 and 25% by weight of the siloxane, based on the quantity of foam resin, is used.

3. A process as claimed in claim 2 in which between 0.20 to 5% by weight of the siloxane is used.

4. A process as claimed in any of claims 1 to 3 in which, in the general formula of claim 1, R represents an aliphatic hydrocarbon radical which contains less than 3 carbon atoms.

5. A process as claimed in claim 4 in which, in the general formula of claim 1, R represents a methyl group.

6. A process as claimed in any of claims 1 to 5 in which, in the general formula of claim 1, R' represents a phenyl radical.

7. A process as claimed in any of claims 1 to 6 in which the polyisocyanate is tolylene-2,4-diisocyanate, tolylene-2,6-diisocyanate or any mixture of these isomers.

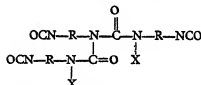
8. A process as claimed in any of claims 1 to 6 in which the polyisocyanate is a polyphenyl-polymethylene-polyisocyanate which has been obtained by aniline-formaldehyde condensation followed by phosgenation.

9. A process as claimed in any of claims 1 to 6 in which the polyisocyanate is a solution of a polyisocyanate containing biuret, allophanate, urethane or isocyanurate groups in a polyisocyanate which is free from such groups.

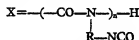
10. A process as claimed in claim 9 in which the polyisocyanate solution contains from 5 to 85% by weight of polyisocyanates containing biuret, allophanate, urethane or isocyanurate groups, based on the total quantity of isocyanate present.

11. A process as claimed in claim 10 in which the polyisocyanate solution contains from 10 to 50% by weight of polyisocyanates which contain biuret, allophanate, urethane or isocyanurate groups.

12. A process as claimed in claim 10 or claim 11 in which the polyisocyanate solution is a solution of a biuret group containing polyisocyanate of the following general formula:



in which R represents an alkylene, cycloalkylene, aralkylene or arylene radical and X represents hydrogen or the group



in which R has the meaning indicated above and  $n$  represents 0 or an integer, in a polyisocyanate which is free from biuret groups.

13. A process as claimed in claim 12 in which, in the general formula of claim 12, R represents a  $\text{C}_1$  to  $\text{C}_6$  alkylene,  $\text{C}_6$  to  $\text{C}_{10}$  cycloalkylene,  $\text{C}_1$  to  $\text{C}_{12}$  aralkylene or  $\text{C}_6$  to  $\text{C}_{10}$  arylene radical.

14. A process as claimed in claim 12 or claim 13 in which  $n$  represents 0 or an integer of from 1 to 5.

15. A process as claimed in any of claims 12 to 14 in which the proportion of biuret polyisocyanates which contain more than 3 isocyanate groups, based on the total quantity of polybiuret isocyanates is at least 20% by weight.

16. A process as claimed in any of claims 1 to 15 in which the polyisocyanate contains up to 20% by weight of monofunctional isocyanate.

17. A process as claimed in any of claims 1 to 16 in which the polyisocyanate contains from 0.3 to 5% by weight of chemically bound emulsifiers.

18. A process as claimed in claim 17 in which the polyisocyanate contains from 0.1 to 2% by weight of chemically bound emulsifiers.

19. A process as claimed in claim 17 or claim 18 in which the emulsifier contains  $-\text{OH}$ , amine, amide,  $-\text{COOH}$ ,  $-\text{SH}$  or urethane groups and is incorporated in the polyisocyanate by reaction with the isocyanate groups.

20. A process as claimed in any of claims 1 to 19 in which the polyether has a molecular weight of between 750 and 10,000.

21. A process as claimed in any of claims 1 to 20 in which at least 10% of the hydroxyl groups of the polyether are primary hydroxyl groups.

22. A process as claimed in claim 20 or claim 21 in which the high molecular weight polyether is used in admixture with low molecular weight compounds which contain active hydrogen atoms.

23. A process as claimed in claim 22 in which the low molecular weight compound is a hydroxyl compound.

24. A process as claimed in any of claims 1 to 21 in which the polyether is used in admixture with up to 50% by weight based on the polyether, of other high molecular weight compounds which contain active hydrogen atoms.

25. A process as claimed in claim 24 in which the polyether is mixed with a polyester, polyacetal, polyester amide or polycarbonate.
26. A process as claimed in any of claims 1 to 25 in which the foam resin is prepared by the one-shot process.
27. A process as claimed in any of claims 1 to 26 in which the reaction mixture contains a catalyst for the production of a foam resin which contains urethane groups.
28. A process as claimed in claim 27 in which the catalyst is a tertiary amine and/or a silamine, an N-substituted aziridine or a hexahydrotriazine, which may be used in combination with an organometallic compound.
29. A process as claimed in any of claims 1 to 28 in which the reaction mixture also contains an additive for regulating the cell structure, an inorganic or organic filler, a dye or a plasticiser.
30. A process for the production of a flame-resistant foam-resin substantially as herein described with reference to any one of the Examples.
31. A flame-resistant foam resin when produced by a process as claimed in any of claims 1 to 30.
32. A resin as claimed in claim 31 which is a cold hardening foam.

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